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**WO 2004/026509 A1**

(54) Title: COATED METALLURGICAL PARTICLES

(57) **Abstract:** The present invention relates to a method of coating hard particles with a metal. The method comprises the sequential steps of : - (i) forming an aqueous slurry of the hard particles, (ii) adding to the slurry an aqueous solution of one or more salts of the metal, said solution having a molality of from 0.1m to 1.6m, (iii) adjusting the pH of the slurry/metal salt solution to between 7 and 14, whereby to coat the hard particles with the metal salt, (iv) heating the metal salt-coated particle slurry to an elevated temperature at an elevated pressure to convert said metal salt to a metal oxide, oxidehydroxide or hydroxide and (v) reducing the metal oxide, oxidehydroxide or hydroxide at said elevated temperature and pressure to the constituent metal, whereby to form said metal coated hard particles, wherein the hard particles are one or more of a carbide, carbonitride and a nitride of one or more of tungsten, titanium, tantalum, niobium, molybdenum, chromium, vanadium, zirconium and hafnium, and wherein said metal is one or more of cobalt, nickel and iron.

## COATED METALLURGICAL PARTICLES

The present invention relates to a method of coating metallurgical particles with a binder metal and to the particles formed thereby.

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As a preliminary stage in the powder metallurgical manufacture of cemented carbides or cermets, the hard carbides, carbonitrides and/or nitrides of metals such as tungsten, titanium, tantalum, niobium, molybdenum, chromium, vanadium, zirconium and hafnium (hereinafter referred to as "hard particles"), are mixed with a suitable binder metal (typically cobalt, nickel, iron or a combination of two or more of these). In order to secure the best mechanical properties in the final, compacted and sintered alloy it is desirable to achieve as uniform mixing as possible. Conventionally, this has been carried out by milling together the constituent powders: in ball, rod or attritor type comminution mills, using hardmetal milling bodies and carrier liquids such as water, ethanol, acetone or hexane. The resultant slurry can have suitable lubricants added (e.g. paraffin wax, polyethylene glycol etc.), and be dried and agglomerated by known methods (e.g. spray drying) to form free flowing agglomerates. Such agglomerates are suitable for compaction in automatic presses to form geometries which in turn can be sintered in a gaseous atmosphere or vacuum to form finished or semi-finished components for use as tools or wear-parts. This process works satisfactorily for hard particle grain sizes from 0.8 to 5  $\mu\text{m}$  but outside this range problems occur. With finer grain-sizes the need to admix with binder metal powders at least as fine as the hard particles results in metal powders which pose health and safety problems due to dust and pyrophoricity. Furthermore, the well known inefficiency of mechanical mills with fine powders results in excessively long milling times. With larger grain sizes the milling process becomes too efficient, comminuting the hard particles in addition to mixing.

A number of alternative methods have been suggested to overcome the above problems with milling:

- 1) adding cobalt (as binder metal) to the hard particles as a halide salt solution, drying and subsequently reducing the product by passing it through a furnace with a reducing atmosphere (e.g. hydrogen or forming gas) to convert the halide to the metal.

2) adding the binder metal as an oxide, such that its highly friable nature greatly accelerates intermixing, together with finely divided carbon. The resultant mixed powder must then be passed through a furnace with an inert (e.g. nitrogen or argon), or reducing (e.g. hydrogen or forming gas) atmosphere to convert the oxide to the metal.

3) forming a slurry of the hard particles in a suitable solvent into which the binder metal is dissolved as a metal salt (e.g. acetate, chloride etc.), evaporating the solvent (usually with agitation), and finely precipitating the binder metal salt on and among the hard particles. This dried mixture must then be furnace treated as in (1) above.

4) as in (1) above, except that the dissolved binder phase is chemically precipitated (as for example an oxalate or malate etc.), before being furnace treated.

In each of the above cases, the product must still be mixed uniformly with lubricant and agglomerated to convert it into a material suitable for use. Thus the above processes inevitably result in greater costs than the standard milling methods.

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Other methods have been aimed at directly coating the hard particles with the binder phase for example:

1) electrolytically plating the hard particles with cobalt. Whilst this appears to give satisfactory results, the difficulties of maintaining electrical contact with the very large numbers of particles necessary for practical purposes renders the technique unusable.

2) electroless plating of the hard particles with cobalt. In this process a slurry of the hard particles and an aqueous solution of cobalt salt or salts (e.g. cobalt chloride, cobalt sulphate, cobalt ammonium sulphate etc.) is treated with a chemical reducing agent, this may be:

(i) salts containing hypophosphite or borohydride. These leave residues in the cobalt of phosphorous and boron respectively. Whilst such residues may be

acceptable, or even desirable, in certain applications, their presence in sintered hardmetal is known to be deleterious.

(ii) chemical reductants such as hydrazine or formaldehyde. These are both expensive, and pose serious health, safety and environmental risks.

5 (iii) monoethylene glycol or other polyols. Reaction products from the breakdown of the reducing agent accumulate in the mother liquor, and their disposal requires incineration or similar treatment.

(iv) direct reduction with hydrogen at elevated temperature and pressure.

Whilst this process operates satisfactorily for nickel, the nucleation and growth of  
10 continuous cobalt deposits has only been achieved by using nucleation agents such as sulphides and cyanides, both of which are hazardous, or organic catalysts such as thioacetamide (a known carcinogen), or by pretreating the hard particles with an activator such as palladium chloride (an expensive noble metal), and/or by  
precoating with nickel (which may or may not be a desired constituent of the binder  
15 phase).

It is an object of the present invention to provide a novel process for the production of coated hard particles which obviates or mitigates one or more of the problems associated with the prior art methods.

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According to the present invention, there is provided a method of coating hard particles with a metal, said method comprising the sequential steps of:-

(i) forming an aqueous slurry of the hard particles,

(ii) adding to the slurry an aqueous solution of one or more salts of the metal,  
25 said solution having a molality of from 0.1m to 1.6m,

(iii) adjusting the pH of the slurry/metal salt solution to between 7 and 14, whereby to coat the hard particles with the metal salt,

(iv) heating the metal salt-coated particle slurry to an elevated temperature at an elevated pressure to convert said metal salt to a metal oxide, oxidehydroxide or  
30 hydroxide and

(v) reducing the metal oxide, oxidehydroxide or hydroxide at said elevated temperature and pressure to the constituent metal, whereby to form said metal coated hard particles,

wherein the hard particles are one or more of a carbide, carbonitride and a nitride of one or more of tungsten, titanium, tantalum, niobium, molybdenum, chromium, vanadium, zirconium and hafnium, and  
wherein said metal is one or more of cobalt, nickel and iron.

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Surprisingly, the inventors have discovered that under the above specified conditions, the binder metal salt (as an ionic metal complex) is adsorbed uniformly onto the surfaces of the hard particles after step (iii). Such uniformity of coating is not possible using prior art methods.

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Preferably, the method is effected to produce a coating of less than 1  $\mu\text{m}$  thickness. The coating may be a continuous coating in which the surfaces of substantially all the particles are completely covered by the coating, or a partial coating in which parts of the surfaces of a significant number of the particles remain uncoated.

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The salt used in step (ii) may be any water soluble salt of the metal and is preferably selected from one or more of a chloride, an acetate, and hydrates thereof. Highly preferred examples include cobalt (II) chloride, cobalt (II) or (III) acetate, and cobalt (II) acetate tetrahydrate. Preferably the molality of the salt(s) is about 0.4m.

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Preferably, step (iii) is effected by the addition of one or more of ammonia, and substituted or unsubstituted quaternary ammonium hydroxides (e.g. ammonium hydroxide, tetramethyl-ammonium hydroxide, diethyl-dimethyl ammonium hydroxide and tetraethyl-ammonium hydroxide). Preferably, the pH is adjusted to  
between about 8 and 9.

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Step (iv) is preferably effected at about 150 to 300°C and more preferably about 200°C. The preferred pressure range for step (iv) is 25-35 bar (2.5-3 MPa). In a preferred embodiment, step (iv) (and preferably step (v)) is effected in an autoclave,  
in which case the pressure is preferably autogenous pressure. Preferably, the slurry  
is stirred for at least a part of the duration of step (iv). Preferably, step (iv) is  
effected for up to about 3 hours, preferably at a heating rate of about 1°C/minute.

30

Preferably, step (v) is effected by introducing hydrogen gas into the slurry. More  
preferably, hydrogen is added at a partial pressure of from 10 to 50 bar (1 to 5 MPa)

35

and most preferably at about 30 bar (3 MPa). Preferably, step (v) is effected for about 2 hours.

5 The present invention also relates to coated hard particles producible by the method of the present invention, and to a compacted and sintered component comprising such hard particles.

Examples of the invention will now be described by way of example only.

10 The hard particles are formed into an aqueous slurry where the pH is controlled between 7 and 14. If the hard particles are agglomerated, deagglomeration is carried out by techniques well known in the art. The control of the pH may be achieved by additions of ammonia, and/or quaternary hydroxides. To this slurry is added an aqueous solution of a suitable salt/salts of the binder metal(s) with a molality of  
15 between 0.1m and 1.6m. As previously mentioned, the binder metal salt is adsorbed uniformly onto the surfaces of the hard particles after step (iii). That this is the case is evidenced by a change in zeta-potential of tungsten carbide when treated with a cobalt salt, indicating that the normally acidic nature of the tungsten carbide surface in aqueous solution has been changed to a basic nature typical of the cobalt  
20 complex.

The hard particle/metal salt mixture is then placed in an autoclave and heated, whilst stirring at its autogenous pressure. Hydrogen is then admitted to the autoclave at the specified pressure and for the specified duration.

25 The autoclave is then cooled, depressurised and purged of residual hydrogen. The now coated particles are separated from the slurry by sedimentation, or filtration, reslurried with, for example, water, alcohol, or a mixture of both mixed with a suitable pressing lubricant, such as polyethylene glycol, and spray dried to give the  
30 desired agglomerated powder.

Approximately 99% of the initial binder metal is reduced to the final product as a finely dispersed metal adherent to the hard particles, without addition of the previously mentioned activation and/or nucleation agents, the use of which is  
35 circumvented by the heterocoagulation step. The remaining 1% of the initial binder

metal stays in solution in the aqueous phase after filtration. This can be re-used in a subsequent process batch, there being no deleterious or harmful breakdown or by-products, as only water, carbon dioxide and nitrogen are generated,

5     Example 1

94g of tungsten carbide powder with a grain-size of 0.4  $\mu\text{m}$  was mixed at room temperature into a slurry with a 0.4m solution of cobalt II acetate, corresponding to a 6g addition of cobalt. Whilst stirring the slurry, 0.880 ammonia solution was added to bring the solution to pH9. Stirring was continued for 30 minutes, after  
10    which the slurry was placed in an autoclave, which was closed and purged with inert gas (nitrogen or argon). The temperature was then increased to 200°C, at autogenous pressure, after which hydrogen was introduced to maintain a pressure of 30 bar (3 MPa) for 2 hours. The autoclave was allowed to cool and depressurise, and then purged with inert gas. The slurry was emptied from the autoclave and the  
15    solid phase separated by sedimentation and decantation, followed by washing and drying.

Analysis of the resultant powder showed it to contain 6% of cobalt as metal. The powder was then mixed with a suitable pressing lubricant, such as paraffin wax, or  
20    polyethylene glycol as is standard in the industry, pressed in a die and subsequently de-lubricated and sintered in a vacuum furnace at 1410°C. Metallurgical and high resolution metallographic examination showed excellent cobalt distribution and the absence of tungsten carbide grain contiguity, cobalt lakes or porosity.

25    Example 2

90g of tungsten carbide powder with a grain-size of 8  $\mu\text{m}$  was mixed at room temperature into a slurry with a 0.4m solution of cobalt (II) acetate and a 0.4m solution of nickel (II) acetate, corresponding to an 8g addition of cobalt and 2g addition of nickel. Subsequent treatment was as described for Example 1 above.

30

Analysis of the resultant powder showed it to contain 8% cobalt and 2% nickel as metal. The powder was then mixed with a suitable pressing lubricant, pressed in a die and subsequently de-lubricated and sintered in a vacuum furnace at 1450°C. Metallurgical and high resolution metallographic examination showed excellent

cobalt distribution and absence of tungsten carbide grain contiguity, binder-phase lakes or porosity.

### Example 3

- 5 91.2g of tungsten carbide powder with a grain-size of 0.2  $\mu\text{m}$  together with 0.3g of vanadium carbide with a grain-size of 0.3  $\mu\text{m}$  and 0.5g chromium carbide with a grain-size of 0.3  $\mu\text{m}$  were mixed at room temperature into a slurry with a 0.4m solution of cobalt II acetate, corresponding to an 8g addition of cobalt. Subsequent treatment was as described for example 1.
- 10 Analysis of the resultant powder showed it to contain 8% cobalt as metal. The powder was then mixed with a suitable pressing lubricant, pressed in a die and subsequently de-lubricated and sintered in a vacuum furnace at 1360°C. Metallurgical and high resolution metallographic examination showed excellent cobalt distribution and absence of tungsten carbide grain contiguity, cobalt lakes or
- 15 porosity. The average sintered grain-size was less than 0.4  $\mu\text{m}$  with an average of less than one grain over 2  $\mu\text{m}$  per observed field at 1500X.

## CLAIMS:

1. A method of coating hard particles with a metal, said method comprising the sequential steps of: -
- 5 (i) forming an aqueous slurry of the hard particles,  
(ii) adding to the slurry an aqueous solution of one or more salts of the metal, said solution having a molality of from 0.1m to 1.6m,  
(iii) adjusting the pH of the slurry/metal salt solution to between 7 and 14, whereby to coat the hard particles with the metal salt,
- 10 (iv) heating the metal salt-coated particle slurry to an elevated temperature at an elevated pressure to convert said metal salt to a metal oxide, oxidehydroxide or hydroxide and  
(v) reducing the metal oxide, oxidehydroxide or hydroxide at said elevated temperature and pressure to the constituent metal, whereby to form said metal
- 15 coated hard particles, wherein the hard particles are one or more of a carbide, carbonitride and a nitride of one or more of tungsten, titanium, tantalum, niobium, molybdenum, chromium, vanadium, zirconium and hafnium, and wherein said metal is one or more of cobalt, nickel and iron.
- 20 2. A method as claimed in Claim 1, wherein the method is effected to produce a coating of less than 1  $\mu\text{m}$  thickness.
3. A method as claimed in Claim 1 or 2, wherein the coating is a continuous coating in which the surfaces of substantially all the particles are completely covered by the
- 25 coating.
4. A method as claimed in any preceding claim wherein the salt used in step (ii) is a water soluble salt of the metal preferably selected from one or more of a chloride, an acetate, and hydrates thereof.
- 30 5. A method as claimed in any preceding claim wherein the molality of the salt(s) is about 0.4m.

6. A method as claimed in any preceding claim wherein step (iii) is effected by the addition of one or more of ammonia, and substituted or unsubstituted quaternary ammonium hydroxides
- 5     7. A method as claimed in any preceding claim wherein, the pH is adjusted in step (iii) to between about 8 and 9.
8. A method as claimed in any preceding claim wherein Step (iv) is effected at about 150 to 300°C.
- 10     9. A method as claimed in any preceding claim wherein the pressure range for step (iv) is 2.5-3.5 MPa.
- 15     10. A method as claimed in any preceding claim wherein steps (iv) and (v) are effected in an autoclave.
11. A method as claimed in any preceding claim wherein the slurry is stirred for at least a part of the duration of step (iv).
- 20     12. A method as claimed in any preceding claim wherein step (iv) is effected for up to about 3 hours, preferably at a heating rate of about 1°C/minute.
13. A method as claimed in any preceding claim wherein step (v) is effected by introducing hydrogen gas into the slurry
- 25     14. A method as claimed in Claim 13 wherein hydrogen is added at a partial pressure of from 1 to 5 MPa.
15. A method as claimed in any preceding claim wherein step (v) is effected for about 2 hours.
- 30     16. A method substantially as hereinbefore described with reference to any of Examples 1 to 3.
- 35     17. Hard particles producible by the method of anyone of Claims 1 to 16.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 03/01432

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>				
<b>IPC7: B22F 1/02, C23C 18/00, C23C 18/34, C23C 18/08</b> According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b>				
Minimum documentation searched (classification system followed by classification symbols)				
<b>IPC7: B22F, C23C</b>				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
<b>SE,DK,FI,NO classes as above</b>				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)				
<b>EPO-INTERNAL, WPI DATA, PAJ</b>				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	<b>GB 1378958 A (SHERRITT GORDON MINES LIMITED),</b> <b>2 January 1975 (02.01.75), page 1,</b> <b>line 23 - page 3, line 31; page 3,</b> <b>line 92 - line 113</b> <div style="text-align: center;">--</div>	1-17		
X	<b>WO 9624454 A1 (SANDVIK AB), 15 August 1996</b> <b>(15.08.96), page 3, line 24 - page 6, line 12</b> <div style="text-align: center;">--</div>	17		
A	<div style="text-align: center;">--</div>	1-16		
X	<b>US 2119488 A (HENRY N. PADOWICZ), 31 May 1938</b> <b>(31.05.38), page 1, line 26 - line 41</b> <div style="text-align: center;">--</div>	17		
A	<div style="text-align: center;">--</div>	1-16		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; border: none;">           * Special categories of cited documents:            "A" document defining the general state of the art which is not considered to be of particular relevance            "E" earlier application or patent but published on or after the international filing date            "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)            "O" document referring to an oral disclosure, use, exhibition or other means            "P" document published prior to the international filing date but later than the priority date claimed         </td> <td style="width: 50%; vertical-align: top; border: none;">           "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention            "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone            "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art            "&amp;" document member of the same patent family         </td> </tr> </table>			* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
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Date of the actual completion of the international search		Date of mailing of the international search report		
<b>9 December 2003</b>		<b>22 -12- 2003</b>		
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86		Authorized officer  <b>Ingrid Grundfelt/MP</b> Telephone No. +46 8 782 25 00		

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 03/01432

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

31/10/03

International application No.

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